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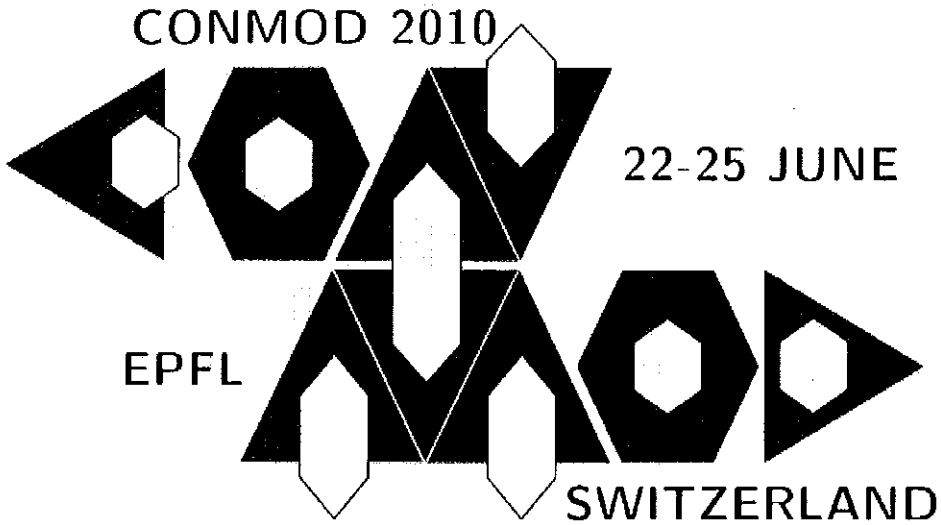

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3D simulation of the leaching of cement-based materials in order to compare different leaching tests

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Leaching of cement-based materials is a complex process that depends on both the material intrinsic properties and the leaching test. The microstructure and cement-type of the material are typical examples of the former whereas the later consist of solution pH and composition, solution renewal rate and the liquid/solid volume ratio. As most of the tests are not normalized, this leads to a diversity of results in terms of alteration layer thicknesses and leaching kinetics. As a consequence, it is often difficult to compare and transpose experimental data from one experience to the other. 1D reactive transport modeling has proven to be adequate to simulate the coupling between diffusion, dissolution / precipitation and sorption processes that take place during leaching. The aim of this study is to demonstrate the usefulness of 3D reactive transport modeling to accurately simulate the features of the leaching device features, which is essential to compare results obtained by different leaching tests. Such simulations also enable to assess the mutual interaction between samples if the device contains several of them. Additionally, these simulations represent an interesting numerical tool in order to design new or complementary leaching tests.

1. Introduction

The degradation of cement-based materials depends on many factors. Some of them do not depend on the experimental device as the material composition, temperature, pH and solution composition [1-5]. Other parameters such as the solution renewal rate and the liquid/solid volume ratio are strictly related to the experimental device. The variability of parameters leads to a diversity of results in terms of portlandite dissolution front, flux of Ca ions and thus, globally, in terms of leaching kinetics. Let's take the example of the leaching of Portland cement pastes. Using a leaching solution of pH 11.5, Revertegat et al. 1992 [6] measured a degraded thickness of 1.2 mm after 36 months while Adenot et al. 1996 [7] measured a thickness of 1.91 mm after 8.5 months. Moreover, a thickness of 1.5 mm was observed by Moranville et al 2004 [4] after 114 days of alteration for a leaching solution of pH 7.

As most of the tests are not normalized, it is difficult to compare different studies, even when they only differ by a single parameter such as temperature, duration of the experiment, pH or hydrodynamic conditions. Considerable progress has been made in the field of reactive transport models and computers are more and more powerful. This offers the possibility of simulating geochemical systems with very complex geometry and hydrodynamic context. Therefore, reactive transport modeling can be used to compare data from literature. Provided we can correctly simulate a leaching experience with its associated device, it is possible to simulate the same experience for another device and eventually compare the results.

After a short description of the mechanisms involved in the degradation of cement paste, we present a reactive transport calculation in 3D-cylindrical geometry in a view of comparing leaching results obtained with the same brine and cement pastes but leached according to two different devices.

2. Leaching of cement-based materials

Many studies have been conducted in order to understand the main mechanisms involved in the leaching of cement paste with pure water [1-4]. Leaching is a combined diffusion–dissolution/precipitation process. The concentration gradients between the pore solution and the leaching solution (generally a pure water) cause diffusion of calcium ions from the pore solution to the surrounding free ion water. The reduction in concentration of calcium ions in the pore solution forces the dissolution of calcium hydroxide (CH) since the pore solution is in

equilibrium with the hydrates of the cement pastes. This results in increased material porosity, and, consequently, in diffusion enhancement.

2.1 Impact of the solution chemical composition

The chemical composition of the leaching solution is of major importance due to its effect on diffusion, as well as dissolution/precipitation reactions. The greater is the concentration gradient between the solution and the pore solution, the greater is the diffusion and the hydrate dissolution. Therefore, pure or deionized water is one of the strongest decalcifying agents of cement-based materials. In contrast, the presence of carbonate ions in the solution decreases the leaching kinetics of the cement matrix [8]. For example, the calcium flux generated by a leaching solution containing $2.5x10^{-3}$ mol/L of $NaHCO_3$ is 40 times lower compared to leaching with deionized water. The degraded layer is consequently lower. After 6 months of leaching, the degraded thickness is 2 mm for pure water but 0.3 mm with a carbonated water. In addition, the mineralogy and texture of solids are modified by the precipitation of calcium carbonate in the later case: the solid/liquid interface consists mainly of a dense calcite layer, which reduces the porosity and, therefore, the diffusivity of the material.

The pH of the leaching solution also greatly influences the degradation kinetics [9]. The concentration gradient between the pore and the leaching solutions leads to the diffusion of hydroxyl ions. Since the pore solution of cement paste has a pH value around 13, the lower the pH of the solution is, the greater the OH^- concentration gradient and the dissolution rate are.

2.2 Impact of material microstructure

The diffusion coefficient and the leaching kinetics depend on the microstructure. Generally, the diffusivity of cement paste increases with the total porosity. As the porosity increases with the Water/Cement ratio, this means that the degradation should increase with the W/C ratio.

In conclusion, the diversity of experiences in the literature can be explained by the number of parameters influencing the cement paste degradation. Apart from standardized tests, it is scarce to find two studies using the same W/C ratio, leaching solution pH and composition, solution renewal rate or ratio liquid/solid volume (V_l/V_s). While some of these parameters can be taken into account by a 1D modeling, such as temperature and pH effects, 3D modeling is required to take into account factors such as solution renewal rates and V_l/V_s ratios.

3. 3D modeling used to compare leaching tests

Reactive transport calculations were done with 3D-cylindrical geometry in order to compare leaching results obtained on the same cement paste leached in two different cylindrical cells with the same brine at 80 °C.

Three monoliths were placed in each cell. The dimensions of cell 1 are: a 3.8 cm diameter and a 57 cm height (Fig. 1). The dimensions of cell 2 are: a 12 cm diameter of cell 2 and a 36 cm height. Two main differences between the two cells could influence the mechanisms of degradation; the first one is the V_l/V_s ratio, which is 33 in cell 1 and 215 in cell 2. The second difference is the solution renewal rate: 3 L/d and 0.5 L/d in cell 1 and 2, respectively. The composition of the solution (brine) and the cement pastes are given in Tab. 1.

Table 1: Brine and cement paste compositions

Brine	mmolal	Cement paste	Kg/dm^3
Ca^{2+}	3.3	CH	0.33
Cl^-	378	CSH (II)	0.86
HCO_3^-	6	Hydrogarnet	0.16
K^+	34	MonoSulfo	0.25
Mg^{2+}	2	Calcite	0,03
Na^+	343	Porosity	0.28
SO_4^{2-}	2		

3.1 Model feature

The reactive transport code HYTEC [10] was used to simulate the dynamic leaching tests taking into account diffusive transport of solutes and chemical reactions. Transport and chemistry are coupled through a sequential iterative algorithm. In addition, the HYTEC code is strongly coupled, e.g., the effective diffusion coefficients change when mineral precipitation or dissolution modifies the local porosity. Thus, HYTEC accounts for clogging by carbonation, or to the contrary, for porosity increase by leaching of calcium hydroxide. A modified version of the Archie's law, which is implemented in HYTEC, was used in a first attempt at modeling the feedback of chemistry on mass transport:

$$D_e(\omega) = D_e(\omega_0)\left(\frac{\omega - \omega_c}{\omega_0 - \omega_c}\right)^{\alpha} \qquad \text{(Eq.1)}$$

where ω is the porosity and D_e is the effective diffusion coefficient. The parameter ω_c is a critical porosity threshold under which diffusion stops and α is the empirical Archie coefficient ranging from 1.3 for unconsolidated sand to 2.2 for consolidated rocks. A zero porosity threshold and an Archie coefficient of 2 were used in this study.

The modeling grids were made according to the configuration represented in Fig. 1, assuming a cylindrical 3D-geometry. Three monoliths were immersed in each leaching cell and a permanent leachant renewal at a given flow rate applied. The leaching solution is the brine detailed in Tab. 1 (e.g. pH of 7.7).

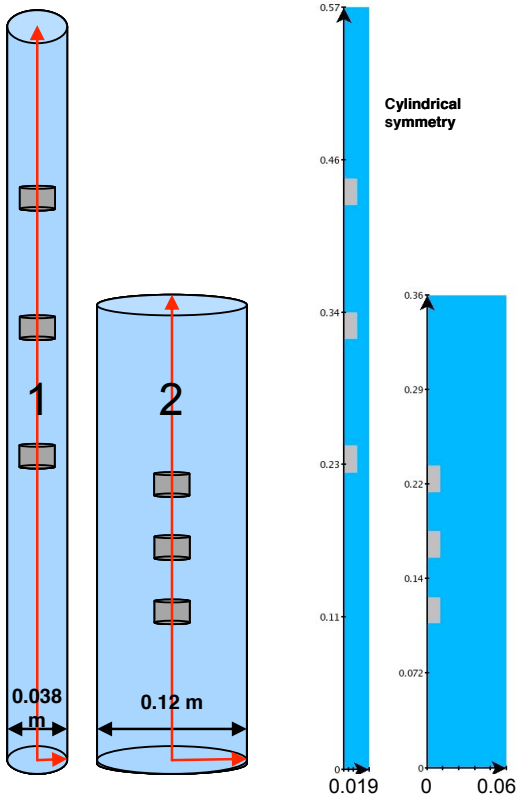

Figure 1: Schematic representation of the dynamic leaching cells (left) and the corresponding cylindrical grids used in the simulations.

3.2 Results

Figure 2 reports the pH data in the leachate over 1 month. Globally, modeling is in good agreement with experiments. The diffusion of hydroxyl ions tends to increase the pH of the brine, which is initially 7.7. The pH increases more significantly in cell 2, to reach a steady-state value of 11, than in cell 1 where the pH remain around 8. This is due to the imposed lower flowrate. In cell 2, the hydroxyl ions leached from cement pastes are evacuated more slowly, which results in increasing the solution pH. In cell 1, the leached hydroxyl ions are

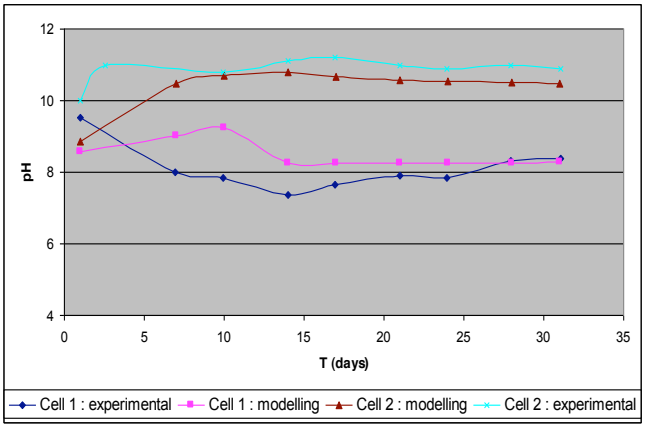

Figure 2: Evolution of pH in the leachate of cells 1 and 2

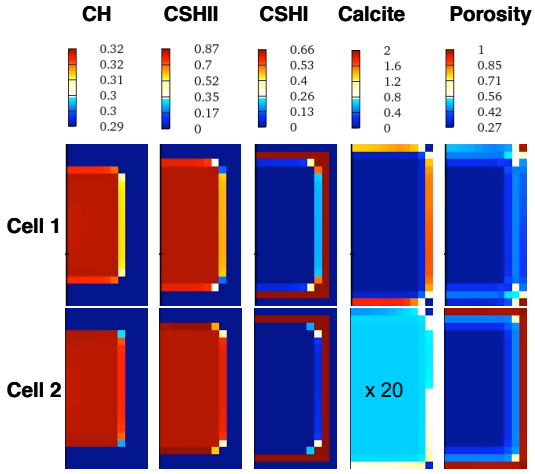

Figure 3: Concentration profiles (in kg/dm^3) and porosity after 30 days.

removed faster due to the higher flowrate.

Figure 3 presents the mineralogical composition of the first monoliths, i.e. the closest to the injection point of the leachant. The altered zone is about 3 mm thick in both cells. As a matter of fact, a dissolution front around 3 mm has been experimentally identified for cell 2 in agreement with the modeling results. The portlandite (CH) is completely dissolved within the first two millimeters and partially within the 3rd mm in the two cells. The decalcification of CSH is highlighted by the transformation of CSH (II) with high Ca/Si ratio to CSH (I) with lower report. In the degraded zone, hydrogarnet dissolves while calcium monosulfoaluminate are formed (data not shown). This phenomenon was experimentally observed in the case of cell 2 [11].

The most important differences between the two cells are related to calcite precipitation and porosity clogging. Indeed, if a calcite layer is formed at the surface of both monoliths, the amount of calcite precipitated at the surface is 50 times greater in cell 1 than in cell 2. The brine flowrate is 6 times higher in cell 1, which means that the inflow of carbonate ion is also significantly larger. This could explain the greater amount of calcite precipitation calculated in cell 1. If the porosity increases in the degraded zone due to the portlandite dissolution in both cells, the formation of calcite on the surface decreases the porosity at the solid/liquid interface in the case of cell 1. The porosity drops from the starting value of 1 in the liquid to 0.45.

4. Conclusions

3D reactive transport modeling was used to compare two experimental devices using the same brine and the same cement pastes. The difference in flowrate and V_l/V_s ratio induces a significant difference in pH between the two cells. The higher flowrate of the cell 1 stabilizes the pH around 8 (against 11 in cell 2). This suggests that the first device (cell 1) is more deleterious. On the contrary, the inflow of carbonate ions is larger in cell 1 enhancing calcite precipitation and porosity decrease. Since the effectiveness of a calcite layer to protect a cementitious material has been demonstrated [8, 11], the first device (cell 1) is less deleterious than cell 2 with this respect.

The interest of such an approach is either to reduce the number of experiments required to study various scenarios of degradation or to compare an experimental result to another one from the literature obtained in other experimental conditions.

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